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(54) STRUCTURAL MATERIAL AND PROCESS FOR ITS PRODUCTION.

(57) A structural material having a light weight and excellent strength and bending modulus, which comprises a polyamide resin reinforced with a reinforcing material of continuous filaments and/or long fibers. This material can be produced according to the monomer casting method by arranging the fibrous reinforcing material in a predetermined form, placing the arranged material in a mold, introducing a molten ω-lactam containing a polymerization catalyst and an initiator thereinto, and heating the mold to polymerize the monomer into a polyamide resin.

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Croydon Printing Company Ltd

SPECIFICATION

Structural Material and Process for its Production.

FIELD OF INVENTION

This invention relates to a structural material suited to be used in racket frame for tennis, squash, badminton or the like, pole for tent frame, pipe for structural material, buried earth pipe, block, fishing rod or the like, and a method of fabricating the same.

BACKGROUND OF THE INVENTION

Fiber reinforced composite materials conventionally used as structural materials for building materials or sports articles include those prepared by adding short fiber reinforced materials to a thermoplastic resin used as the matrix, or other prepared by adding long filament reinforced materials to a thermoset resin used as the matrix.

These materials, however, involve the following problems in the forming property, strength, heat resistance and fatigue characteristic, and superior fiber reinforced composite materials have been demanded.

For example, reinforced plastic poles are recently sold on market as the pole for mountaineering tent, but they have their problems as stated below, and they are presently used

partly only in a field of less rugged conditions such as picnic tent.

That is, in the composition of these reinforced plastic poles, the reinforced fibers are composed of glass, carbon, or aromatic polyamide, and the matrix is made of epoxy, polyester or other thermoset resin. The most widely employed method of fabricating reinforced plastic poles is the so-called "drawing pipe" method which is to impregnate glass fibers with polyester resin, and continuously lead into the hardening bath to be hardened. In other versions, fibers are processed by filament winding (F/W) process, not limited in the axial direction, or ABS resin or other thermoplastic resins are used as the padding or covering material, but anyway the matrix of reinforced fibers is always thermoset resin such as polyester and epoxy.

These thermoset resins are, by nature, brittle, and are easily broken when bent sharply like a tent pole. Or if the rigidity is lowered to allow a large deflection in practical usage problems occur in the aspects of habitability or resistance to wind pressure. In particular, when several poles are joined together, stress is concentrated at joints, and majority of breakdown is originated from the joint. However, in the continuous drawing method, since its section is uniform, it is difficult to reinforce only the joint part integrally. Or in the case of F/W process, it is difficult

to vary the complicated joint shape or outside diameter, and there are serious problems such as fluctuations of dimensional precision and performance derived form the nonuniformity of tape wrapping.

On the other hand, in the composition of fiber reinforced plastic used as the material of golf club shaft, the reinforced fibers are composed of carbon, glass, aromatic polyamide, boron or the like, and the resin matrix is made of epoxy, polyester or other thermoset resin. All of them share a main feature of lightness of weight as compared with metallic shaft, and also provide the following merits.

1) The head speed when swinging increases.

2) Even a less powerful golfer can swing easily.

Fabrication methods of this kind of shaft are roughly divided into two types as follows.

(1) Filament winding (F/W) method

a continuous filament is impregnated with resin, and is wound on a mandrell at a specified angle in the axial direction.

(2) Sheet winding method

A cloth prepregnated with resin is wound on the mandrel.

In both (1) and (2), after forming on the mandrel, the material is wrapped by heat-shrink tape, and is heated in a hardening furnace.

In these methods, however, the dimensional precision when forming the material is not sufficient, and the pressure when hardening depends on the tightening force of the wrapped tape, so that the dimensional precision of product is limited. Besides, since marks of wrapping tape are left over on the product surface, it is necessary to finish the surface by buffing with centerless grinder or the like, so that part of surface fibers is shaved off. And it is also difficult to vary the complicated shape or outside diameter noncontinuously, and the degree of freedom of design is limited. Furthermore, thermoset resins of epoxy and polyester are more brittle, and may be broken when an impact is applied.

In addition, the following two types are known as the composition of fiber reinforced plastics for racket frame for ball games.

(1) Continuous fiber/resin matrix type

(2) Short fiber of chopped fiber/resin matrix type

In type (1), epoxy, polyester or phenolic thermoset resin is used as resin matrix, and it is impregnated in continuous filament, and heated and pressurized, so that the resin is hardened and molded into a desired shape.

In type (2), the reinforced members are composed of fiber reinforced members of short discontinuous length randomly dispersed in the resin matrix, and this resin may be

either thermoplastic or thermosetting. As the thermoset material, the one shown in (1) is used, and as the thermoplastic material, for example, nylon, polycarbonate, polyphenylene oxide, acetal and other so-called industrial thermoplastics are used. As the molding method, mainly injection molding is employed.

On the other hand, as the characteristics required in rackets, usually, toughness, rigidity and resilience are known. As for toughness, since the toughness of matrix resin of type (1) is inferior, expensive carbon fibers or other reinforced fibers are used usually by 60 to 70 wt.% in order to obtain a required toughness. Since this is an easy method of obtaining a required strength and desired shape, this method is employed in almost 100 percent in the existing tennis racket frames using reinforced plastics.

In the case of (2), usually, considering the moldability, in particular, fluidity at the time of injection, the molecular weight of matrix resin is kept low. The fiber content is about 30 wt.%, and the fiber length is mostly less than 1 mm (0.2 to 0.3 mm) after pelletizing and injection molding. Since the matrix resin is not high in molecular weight and the length of reinforced fibers is extremely short, improvement of mechanical strength in this composition is not expected. Therefore, if such racket strung with guts is kept in an automobile trunk, for

example, and its internal temperature exceeds 80°C, it is highly possible that the frame may be deformed or broken during use.

To compensate for this defect, it is consequently necessary to increase the wall thickness of racket frame, but since the total weight increases, it is not so practical.

Recently, meanwhile, as the sports are becoming popular as pastime, considerations to sports injuries are required. For example, according to a certain polling, about one third of tennis players claimed to have "experienced pain in the elbow." This is known as tennis elbow, and the player feels pain suddenly in the elbow of the racket holding side without any specific cause. In a racket inferior in vibration absorption property, it is said that the vibration of hitting a ball is transmitted to the elbow to damage the humerous epicondylus. In the continuous filament/resin matrix type (1) which is in the mainstream of the present racket frame materials, since the commonly used epoxy resin and polyester resin are inferior in impact absorption or toughness and high rigidity fibers such as carbon fiber are contained by 60 to 70 wt.% in order to improve flexural modulus, it is considered that the vibration characteristic be inferior.

Incidentally, as technical reports about industrial materials using nylon resins, for example, "Nylon RIM

Development for Automotive Body Panels" (SAE Technical Paper Series 850157, 1985), and "Nylon 6 RIM" (American Chemical Society, 1985) are known, and also an article relating to terminal amine polyether RIM (SAE Technical Paper Series 850155, 1985), an article relating to the future of RIM in America (American Chemical Society, 1985), and an article relating to RIM monomer casting ("Plastics Technology," May 1985 issue) are available, but nothing is mentioned about long filament reinforced products in these papers.

The present invention is devised in the light of the above background, and it is hence a primary object of this invention to present a structural material which is lightweight, excels in strength and flexural modulus, and is large in the degree of freedom of designing of shape and material as compared with that of conventional materials.

DISCLOSURE OF THE INVENTION

The structural material of this invention (a first invention) is characterized by that a polyamide resin reinforced by continuous fiber and/or long filament reinforcing material is used as the base material to form the structure. The method of fabricating the structural material of this invention (a second invention) is a method of fabricating a structural material composed of polyamide resin reinforced by continuous fiber and/or long filament reinforcing

material, in which the long fiber and/or long filament reinforcing material is arranged preliminarily in a desired shape and put in a mold, and a molten ω-lactams containing polymerization catalyst and initiator is poured into the mold, and it is heated to obtain polyamide resin by monomer casting method, thereby forming a structural material.

The monomer used in this invention, ω-lactams, may include the following examples: α-pyrrolidone, α-piperidone, ε-caprolactam, ω-enantolactam, ω-caprilolactam, ω-peralgonolactam, ω-decanolactam, ω-undecanolactam, ω-laurolactam, their c-alkyl substitute-ω-lactam, and mixture of two or more kinds of ω-lactams. However, what is advantageous industrially is e-caprocaltam or ω-laurolactam. And ω-lactams may contain, if necessary, modifying components (soft components).

A soft component possesses in molecule a functional group reacting with an initiator used, and it is a component of low Tg, and usually polyether or liquid polybutadiene possessing functional group is used.

A commercial material used in this invention may be, for example, UX-21 which is a nylon RIM material manufactured by Ube Industries, Ltd. It is composed of component A made of alkali catalyst and caprolactam, and component B made of prepolymer containing soft component and caprolactam.

As the anionic polymerization catalyst used in this invention, sodium hydride (NaH) is preferable, but also other sodium, potassium, lithium hydride and known ω-lactam polymerization catalysts may be used. The content is preferably in a range of 0.1 to 5.0 mol% of ω-lactam.

As the polymerization initiator, N-acetyl-ε-caprolactam is used, but other applicable examples are triallylisocyanurate, N-substitute ethyelene imine derivative, 1,1'-carbonyl visazilidine, oxazoline derivative, 2-(N-phenylbenzimidoyl) acetoanilide, 2-N-morpholino-cyclohexene-1.3-dicarboxysanilide, known isocyanate, carbodimide and similar compounds. The content of the initiator is preferably in a range of 0.05 to 1.0 mol% of ω-lactam. The methods of its addition include:

(A) A method of directly adding and mixing to ω-lactam solution containing anionic polymerization catalyst;

(B) A method of mixing ω-lactam solution containing anionic polymerization catalyst and another ω-lactam solution containing polymerization initiator; and

(C) A method of adding together with anionic polymerization catalyst preliminarily to the solid or liquid ω-lactam. Any method may be employed.

The polymerization temperature is generally preferable in a range of 120 to 200°C, but it is also possible, for special purposes, to polymerize under 120°C or over 200°C.

As the continuous fiber which is a reinforcing material, depending on the applications, carbon fiber, aramide fiber, glass fiber, alumina fiber, silicon carbide fiber, steel wire, amorphous metal fiber and/or their hybrid may be used in a state of cloth, sleeve or roving.

The continuous fibers and/or long filaments are placed in the mold, for example when fabricating a pipe-shaped structural material, by winding a necessary amount around the core, or covering the core as sleeve. To obtain a block-shaped product, it may be preliminarily set in the mold.

In this invention, since the monomer casting method is employed, there is no limitation to the molecular weight in consideration of the molding processability, and a polyamide resin of high molecular weight is obtained, so that the strength, elasticity and thermal distortion temperature are high. So the thickness of the structural material may be reduced, and the weight may be light.

As the material of thermoplastic resin reinforced by long filaments, a so-called stampable sheet is known, and as its nylon version, a sheet composed of nylon resin and continuous glass fiber mat may be considered as an example, but when obtaining a molded product of desired shape by using such stampable sheet, the following problems exist. That is, when a stampable sheet is used as molding material, it

is necessary to handle the heated and melted material sheet outside the mold, and at this time the temperature is as high as 200 to 350°C, and the molten material sheet is very soft and extremely hard to handle. Besides, a heating equipment using far infrared rays is required, and the facility cost is high. Furthermore, the press pressure at the time of molding is very high, about 100 to 300 kg/cm², and the mold and other facilities are expensive. Still more, the reinforcing fibers form relief patterns on the molded product surface, or air bubbles mixed in the heating process of material cannot be forced out completely when molding and are left over on the surface, and the surface finished state is not favorable. Or it is difficult to form thinly or in complicated shape.

Therefore, the method of this invention by monomer casting process seems far more excellent.

In this invention, moreover, since a tough polyamide resin is used instead of brittle thermoset resin, the content of reinforcing fiber may be small, and in particular by using continuous fiber and/or long filament it is possible to reinforce further and decrease the content of reinforcing fibers, so that economy and light weight may be achieved together. In addition, the excellent vibration attenuating characteristic of the polyamide resin used in the matrix resin becomes more notable because the content of

reinforcing fibers is small, so that the racket frame, shaft for ball games, and other structural materials light in weight and excellent in durability and appearance may be obtained.

The structural material by this invention is excellent in lightness of weight, strength, flexural modulus, vibration attenuation characteristic and other properties, because tough polyamide resin, instead of brittle thermoset resin, is used as matrix resin, and it is further reinforced by continuous fiber and/or long filament reinforcing material.

This structural material is easily formed in a desired shape by the fabricating method according to the second invention, in which the fiber reinforcing material is preliminarily placed in a desired shape, and the matrix resin is added to it by monomer casting.

The conventional fiber reinforced composite materials were fabricated by a premix method in which the reinforcing material was premixed with the resin and then formed, and it was difficult to form in a complicated shape generally, while, in this invention, it is easy to form and the degree of freedom of design is great.

BRIEF DESCRIPTION OF THE DRAWINGS.

FIG. 1 to FIG. 5 are sectional views expressing the

embodiments of this invention; FIG. 6 and FIG. 7 are graphs expressing the elasticity and bending strength; FIG. 8 and FIG. 9 are graphs to express the fatigue curve; FIG. 10 is a explanatory diagram of calculating method of damping ratio; FIG. 11 is a front view of a tennis racket frame; FIG. 12 is a sectional view of a conventional product; FIG. 13 is a sectional view of a product by this invention; FIG. 14 is a explanatory diagram of testing method of attenuation characteristic; FIG. 15 and FIG. 16 are graphs to express the attenuation waveform of a reference example and an embodiment; and FIG. 17 is a explanatory diagram of calculating method of damping ratio.

1: mandrel, 10: racket frame, 10a: head, 10b: grip

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiment 1

As shown in FIG. 1, carbon fibers 2 braided at an angle of 25° in the axial direction around a mandrel 1 made of stainless steel were placed in a mold by 35 Wt.%. At this time, a joint 3 was curved at a position where stress was concentrated due to bending deformation to obtain a face contact, and the convex and concave portions were tapered to increase the wall thickness at parts A and B shown in FIG. 2 where breakage often occurred at the joint

of the conventional rectangular section. This mold was heated at 150°C, and was evacuated to 1 mmHg by using a vacuum pump. 100g of ε-caprolactam was heated and melted at 130°C in a 1-liter flask while replacing with nitrogen, and 0.21g of NaH (50% oil-based) was added to react and dissolve completely. At the same time, in another 1-liter flask, 100g of ε-caprolactam was put, and was heated and melted at 130° while similarly replacing with nitrogen, and 0.13g of N-acetyl-ε-caprolactam was added to dissolve completely. In said mold, these lactam mixture solutions were poured simultaneously, and the mold was kept at 150°C for 30 minutes. It was then annealed in a 90°C oil for 2 hours, and heated in boiling water for 3 hours.

As a result, a pipe for structural material 4 excelling in lightness of weight, flexural modulus and bending strength was obtained.

Embodiment 2

The procedure was same as in embodiment 1, except that the outside diameter of the concave portion of joint 3 was increased as shown in FIG. 3 in order to increase the strength at the joint part.

As a result, a pipe for structural material 4 excelling in lightness of weight, flexural modulus and bending strength, same as in embodiment 1, and further reinforced in

the joint was obtained.

Embodiment 3

As shown in FIG. 4, carbon fibers 2 were braided at an angle of 25° in the axial direction around a mandrel 1 made of stainless steel were placed in a mold by 35 wt.%. This mold was heated to 150°C, and evacuated to 1 mmHg by vacuum pump. In a 1-liter flask 100g of ε-caprolactam was heated and melted at 130°C while replacing with nitrogen, and 0.21g of NaH (50% oil-based) was added to react and dissolve completely. At the same time, in another 1-liter flask, 100g of ε-caprolactam was taken, and heated and melted at 130°C while similarly replacing with nitrogen, and 0.13g of N-acetyl-ε-caprolactam was added to dissolve completely. These lactam mixture solutions were simultaneously poured into said mold, and a lid was put on immediately, and the mold was kept at 150°C for 30 minutes.

As a result, a golf club shaft 5 of hollow pipe shape was obtained.

Finally, a persimmon head was attached to the end 6 in FIG. 4 and a rubber grip to the grip part 7, and a product was completed. When actually golf balls were hit, the durability was sufficient.

Embodiment 4

As shown in FIG. 5, the procedure was same as in embodiment 3, except that carbon fibers 2 were arranged so that the wall thickness was smaller in part (part P) of a shaft 5 than in other parts.

By shifting the position of part P to the end 6 or grip 7 side, the position of kick point could be freely designed.

Embodiment 5

The structural material of this invention was fabricated by varying the content of carbon fibers according to the same monomer casting method as in embodiment 1, except that the fiber angle was 15°.

In thus obtained structural materials, the flexural modulus, bending strength, fatigue characteristics, heat resistance, and breakdown energy were investigated, and the results were as shown in FIGs. 6, 7, 8, 9 and TABLES 1, 2. In these diagrams, A refers to the product of this invention , B denotes an epoxy prepreg material, C is a polyamide resin material using short fiber (carbon) reinforcing material, D represents a commercial tennis racket frame made of an epoxy prepreg material, and E is a tennis racket frame of polyamide resin/short fiber (carbon) type. All of B through E are reference examples.

In FIG. 9, the rate of fatigue stress to breakdown strength is plotted on the axis of ordinates, and the load

cycle is given on the axis of abscissas, in which A refers to the structural material (carbon fiber) of this invention formed by monomer casting method, and A' is a composite material (stampable sheet) made from nylon resin using continuous glass fiber mat as reinforcing material.

The test conditions were as follows. A fiber angle was $\pm 15^0$. The test carried out by three-point bending at test speed of 2.5 mm/min for flexural modulus and bending strength. The test span was 100 mm, and the test piece measured 4 mm thick x 10 mm wide x 150 mm long. The method of fatigue test was three-point bending at a constant stress and test frequency of 1 Hz. The fiber angle was at $\pm 15^0$, the test piece dimensions were 4 mm thick x 10 mm wide x 150 mm long, and the test span was 80 mm, the fixed durability limit was 10^5 times.

The breakdown energy was in the same condition as in bending strength. For heat resistance, the holding rate of stiffness (E100/E20, E150/E20) at 100°C (E100) and 150°C (E150) was determined from the stiffness at room temperature (E20). In these tests, type 2050 apparatus by Intesco was used.

To measure the attenuation performance, a test piece measuring 4 mm thick x 10 mm wide x 150 mm long at fiber angle of ±15° was suspended by a string, and was given an impact by an impact hammer, and the acceleration (α) was measured by acceleration pickup to determine α/F by fre-

quency analysis.

The damping ratio (ζ) was calculated by using dynamic analyzer 3562A manufactured by YHP. That is, by frequency analysis of α/F, ζ was determined in the following equation from FIG. 10.

$$\zeta = (1/2) \times (\Delta\omega / \omega n)$$

$$T_0 = Tn / \sqrt{2}$$

The result was 0.0558 in nylon resin (UX-21 being heated and polymerized) without reinforcing fiber, 0.0107 in nylon resin with carbon fibers without surface treatment (fiber angle 17°), 0.0135 in nylon resin with carbon fibers surface treated by nylon surface treating agent (fiber angle 12°), 0.0122 in nylon resin with carbon fibers without surface treatment (fiber angle 19°), 0.0230 in nylon resin (NY66) with 15% carbon fibers, 0.0159 in NY66 with 30% carbon fibers, 0.0098 in epoxy resin with carbon fibers, and 0.0323 in a test piece cut out from a commercial racket frame (Max. 200G PRO).

As clear from these findings, the structural material by this invention was excellent in strength, heat resistance, fatigue characteristic, etc.

Embodiment 6

Braided carbon fibers were wound around a nylon tube which was a synthetic resin tube, by 45 wt.%, and a cloth of

aromatic polyamide resin (tradename KEVLAR49) by 10 wt.%, and they were put in a mold of mid-size tennis racket frame. This mold was heated to 150°C, and evacuated to 1 mmHg by using a vacuum pump. Precisely 300g of ε-caprolactam was heated and melted at 130°C in a 1-liter flask while replacing with nitrogen, and 0.64g of NaH (50% oil based) was added to react and dissolve completely. At the same time, in another 1-liter flask, 300g of ε-caprolactam was put, and was heated and melted at 130°C while similarly replacing with nitrogen, and 0.4g of N-acetyl-ε-caprolactam was added to dissolve completely. These lactam mixture solutions were simultaneously put into said mold, and a lid was immediately put on, and the mold was kept at 150°C for 30 minutes. Its core part 16 was filled with urethan foam, and a grip was attached to a shaft part 10b to manufacture a product as shown in FIG. 4. This tennis racket frame 10 had head part 10a and grip part 10b, and the product weight was 325g. This frame 10 was strung with gut and was used in actual play, and there was no problem in its durability.

The vibration attenuation characteristic of this racket strung with gut is shown in FIG. 16. FIG. 16 is realized by this invention, possessing a section as shown in FIG. 13, in which the filled core 16 is foamed urethane as mentioned above, numeral 15 is a nylon tube, 14 is a surface resin layer (nylon) and 13 is a substrate made of a sleeve of

continuous filament of 45 wt.% carbon fibers and 10 wt.% aromatic polyamide resin fibers (tradename KEVLAR49).

FIG. 12 and FIG.15 are reference examples showing the vibration attenuation waveform of a racket, using foamed urethane as core 12 and having an outside part 13 made of epoxy rein containing 70 wt.% of continuous filaments of carbon fibers being hardened by heating and pressurizing. Numeral 14 is a resin layer (epoxy resin). The racket weighed 340g.

The vibration attenuation waveform was obtained as follows. As shown in FIG. 14, a tennis ball 17 was suspended on a string, and it was dropped by gravity to hit against the center of hitting area of a racket 8 strung with gut which was also suspended on a string with the frame hitting part (head part 10a) upward, and the attenuation of the vibration at this time was received by an accelerometer 19 which was mounted on the grip by way of an aluminum plate 20. And it was observed on a cathode-ray tube as vibration attenuation waveform.

From the attenuation waveforms in FIG. 15 and FIG. 16 thus obtained, the damping ratio ζ was determined in the following equation according to FIG. 17.

$$\zeta = \frac{1}{\pi\ (n-1)} \cdot \ell n \frac{\omega 1}{\omega 2}$$

When the damping ratio was calculated, it was 0.0222 in

FIG. 14, and 0.0[illegible] in FIG. 16. As clear from this fact, the product of this invention was extremely excellent in the vibration attenuation characteristic as compared with conventional products.

Embodiment 7

Component A of UBE Nylon RIM (UX-21) (caprolactam containing alkali catalyst) and component B (caprolactam containing prepolymer) were heated and melted at 90 to 100^{0}C while replacing with nitrogen and components A and B were quickly mixed, poured into carbon fibers (reinforcing material) surface treated with 0.5% methanol solution of Toray AQ Nylon (A-70) and kept at 150^{0}C for 10 minutes.

Using this material, a similar racket frame to the one in embodiment 6 was prepared. The obtained racket frame presented equal or better performances as compared with the product of embodiment 6.

Embodiment 8

The procedure was same as in embodiment 7, except that a cloth was used so as to contain carbon fibers by 30 wt.% as reinforcing fibers. The head wall thickness of frame was 1.5 mm (average). The intrinsic visocity (η) of the resin of this racket frame was 3.07 (solvent m-cresol; according to ISO 307).

Embodiment 9

The procedure was same as in embodiment 8, except that the content of carbon fibers was 70 wt.%, and that the hitting area of frame was 170% larger than that of mid-size, and that the head wall thickness of frame was 1 mm at maximum.

TABLE 1 Heat Resistance

	Embodiment	Short fiber reinforced Nylon 6-6 resin			Long filament reinforced epoxy resin		
		Sheet sample reference example		Racket frame reference example	Sheet sample reference example (A)	(B)	Racket frame reference example
Fiber content [wt.%]	35	15	30	26	60	60	48
Holding rate of flexural modulus at 100°C [%]	82	35	40	54	97	18	43
Holding rate of flexural modulus at 150°C [%]	78	30	35	47	58	10	48

TABLE 2 Breakdown Energy

	Embodiment	Long filament reinforced epoxy resin reference example
Fiber content [wt.%]	35	60
Breakdown energy	650	700

WHAT IS CLAIMED IS:

1. A structural material made of polyamide resin reinforced by continuous fiber and/or long filament reinforcing material.

2. The structural material of claim 1, wherein said fiber reinforcing material is surface treated with nylon surface treating agent which is soluble in alcohol, water or in both water and alcohol.

3. The structural material of claim 1 or 2, wherein the intrinsic viscosity [η] of said polyamide resin is 1.8 or more.

4. The structural material of claim 1, 2, or 3, wherein said polyamide contains 10 to 80 wt.% of continuous fiber reinforcing material and/or long filament reinforcing material.

5. The structural material of any one of claims 1 to 4, wherein the structural material is a bar material.

6. The structural material of any one of claims 1 to 4 wherein the structural material is a tennis racket.

7. A fabricating method of structural material composed of polyamide resin reinforced by continuous fiber and/or long filament reinforcing material according to the monomer casting method comprising steps of arranging said continuous fiber and/or long filament reinforcing material preliminarily in a desired shape, putting into a mold, pouring molten ω-lactams containing

polymerization catalyst and initiator into said mold, heating to obtain polyamide resin, and forming the structural material.

8. The fabricating method of structural material of claim 7, wherein said fiber reinforcing material is preliminarily surface treated with a nylon surface treating agent which is soluble in alcohol, water or in both alcohol and water.

9. The fabricating method of structural material of claim 7, wherein the structural material is a bar material.

10. The fabricating method of structural material of claim 7, wherein the structural material is tennis racket.

FIG. 1

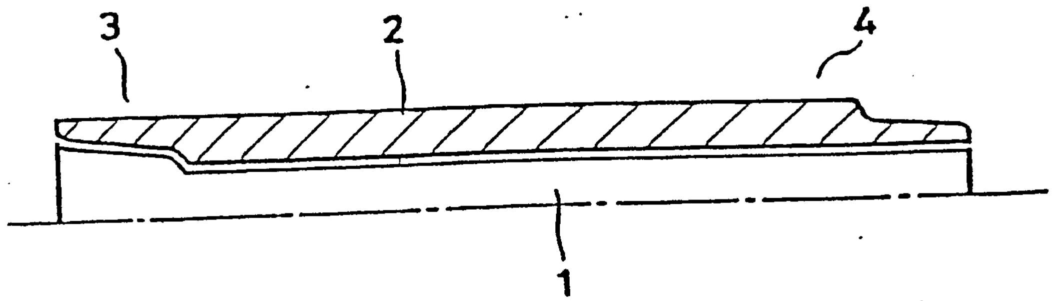


FIG. 2

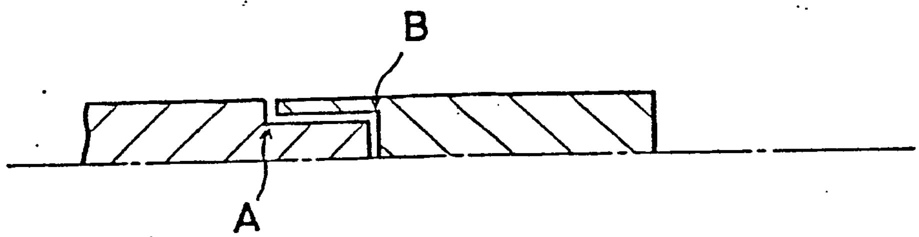


FIG. 3

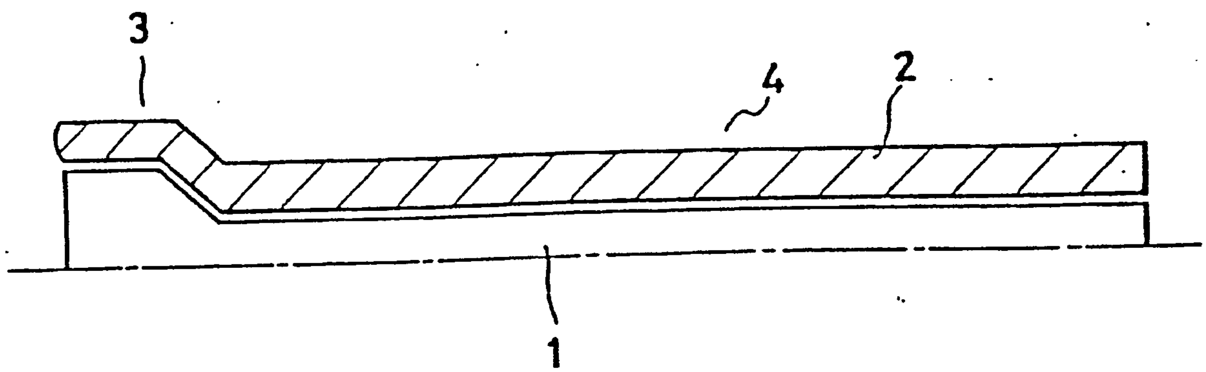


FIG. 4

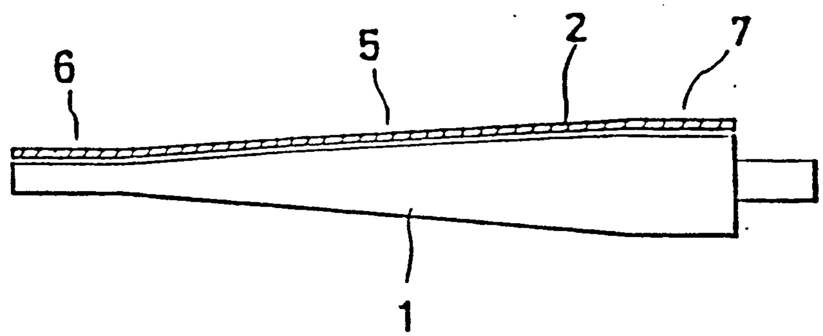


FIG. 5

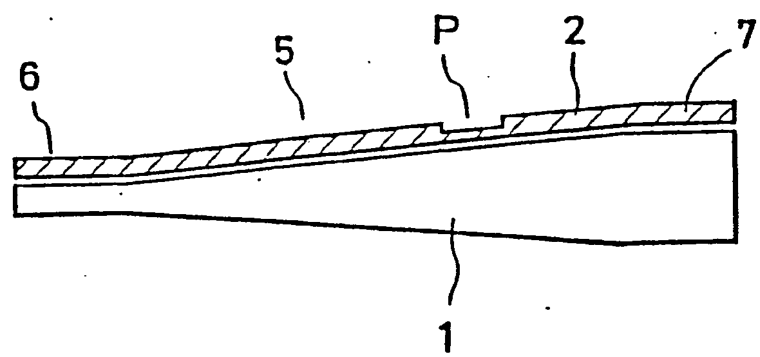


FIG. 6

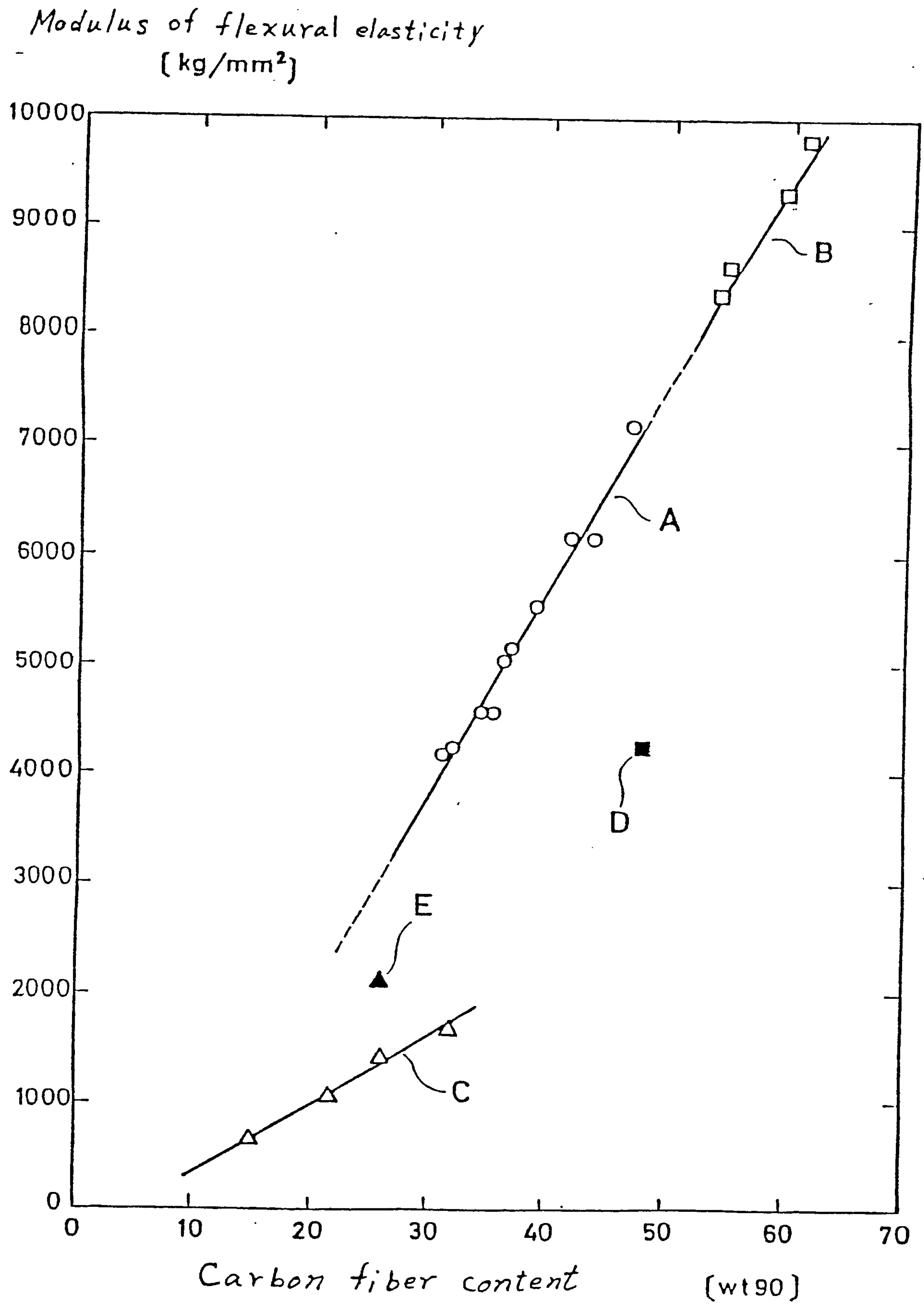
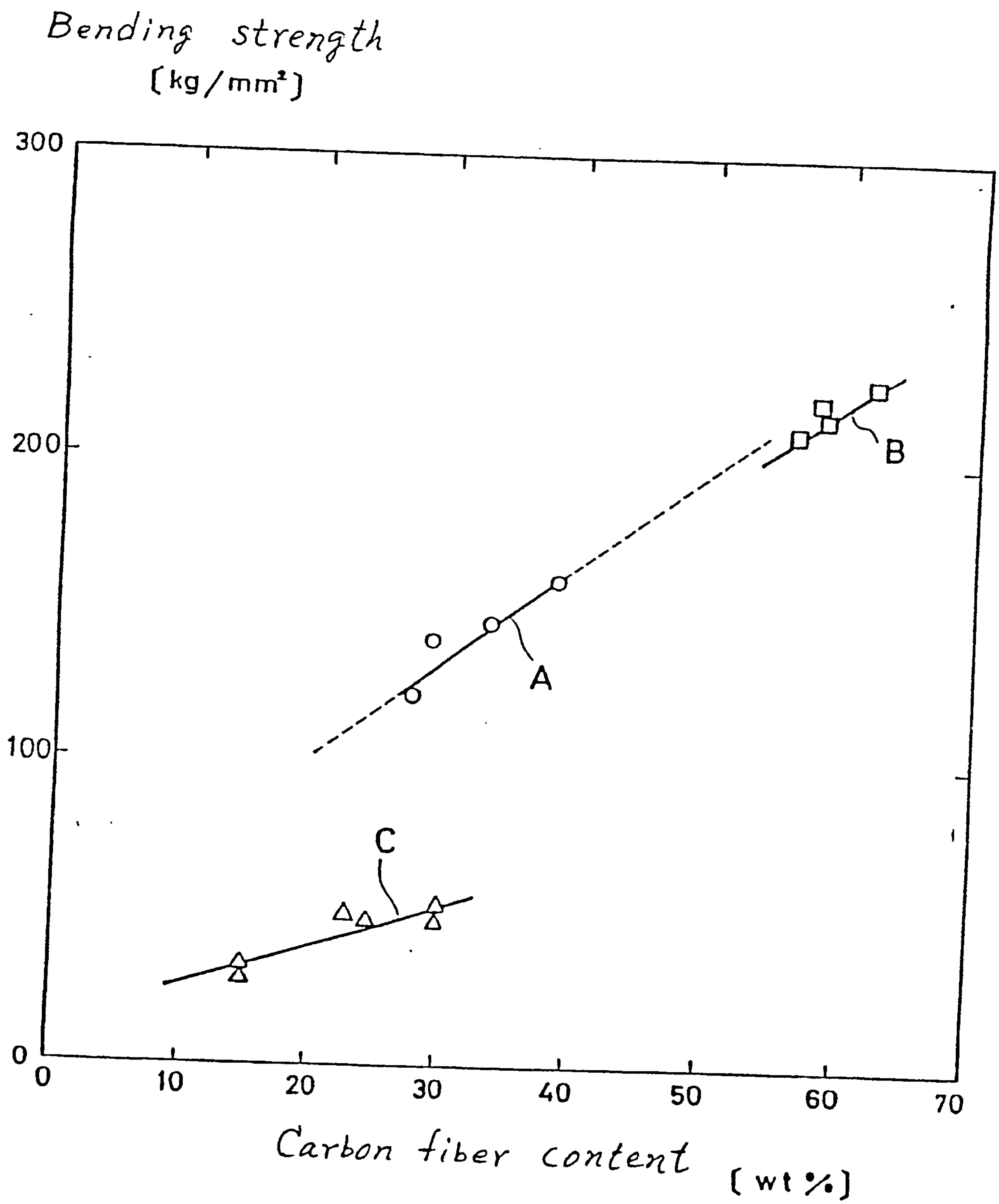
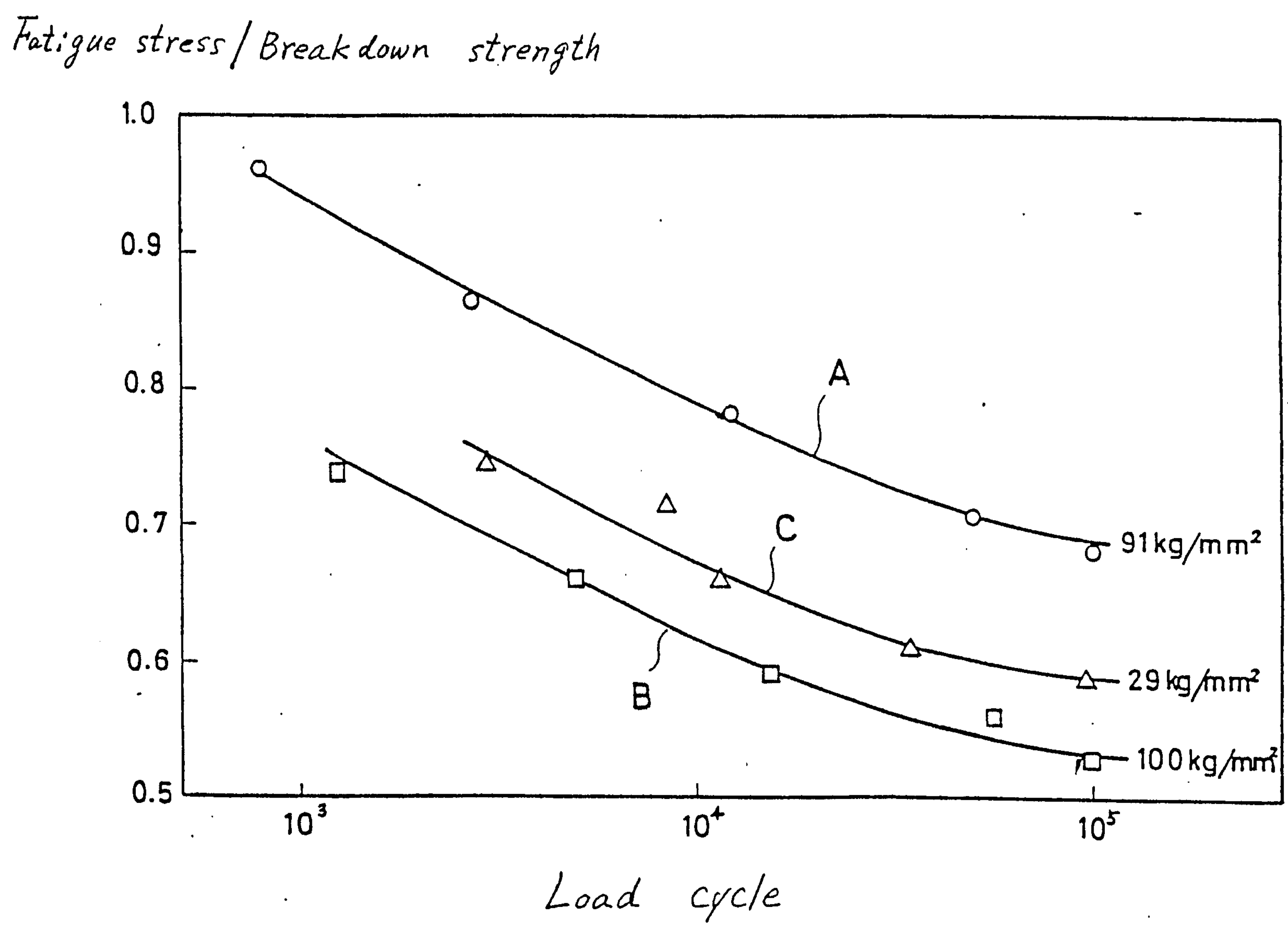

Modulus of flexural elasticity
[kg/mm²]
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
10
20
30
40
50
60
70
A
B
C
D
E
Carbon fiber content
(wt%)

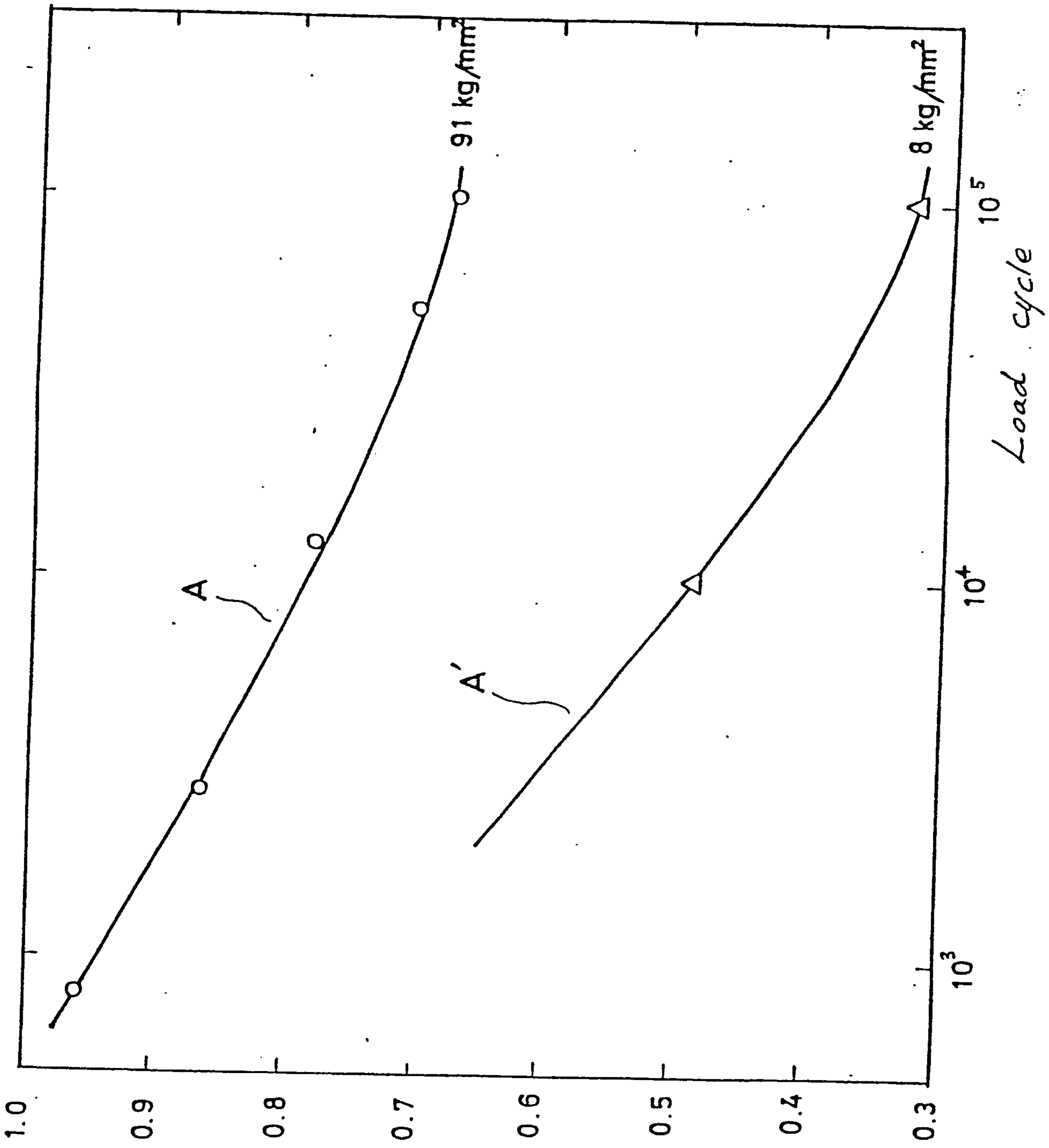
FIG. 7



Bending strength
[kg/mm²]
300
200
100
0
0
10
20
30
40
50
60
70
A
B
C
Carbon fiber content
[wt%]

FIG. 8


Fatigue stress / Breakdown strength
1.0
0.9
0.8
0.7
0.6
0.5
A
B
C
91kg/mm²
29kg/mm²
100kg/mm²
10^3
10^4
10^5
Load cycle



Fatigue stress/ Breakdown strength

FIG. 9

FIG. 10

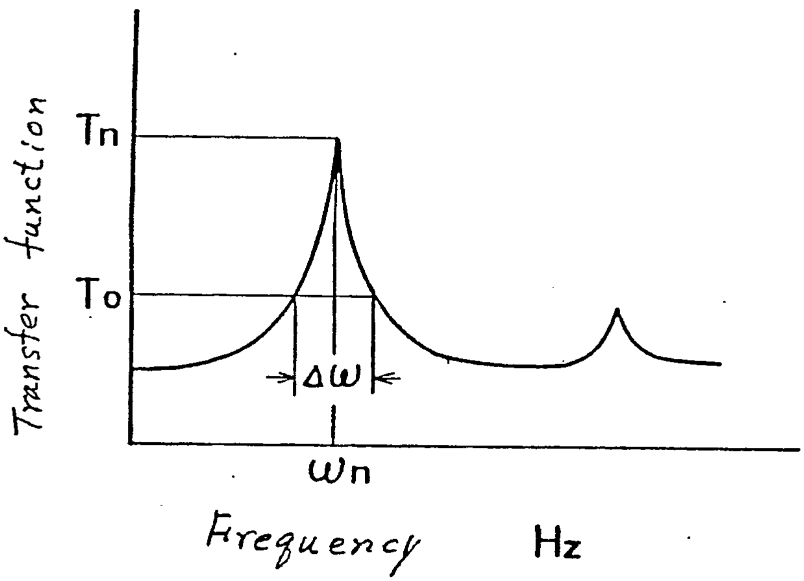


FIG. 17

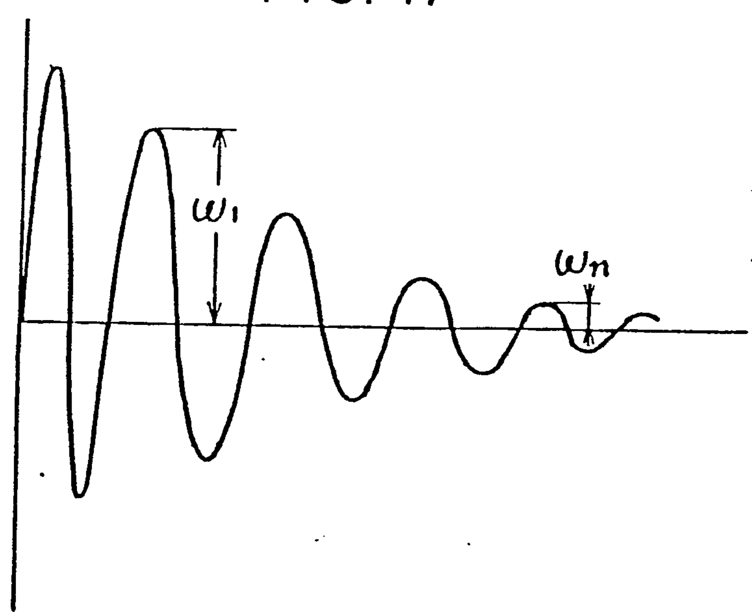


FIG. 11

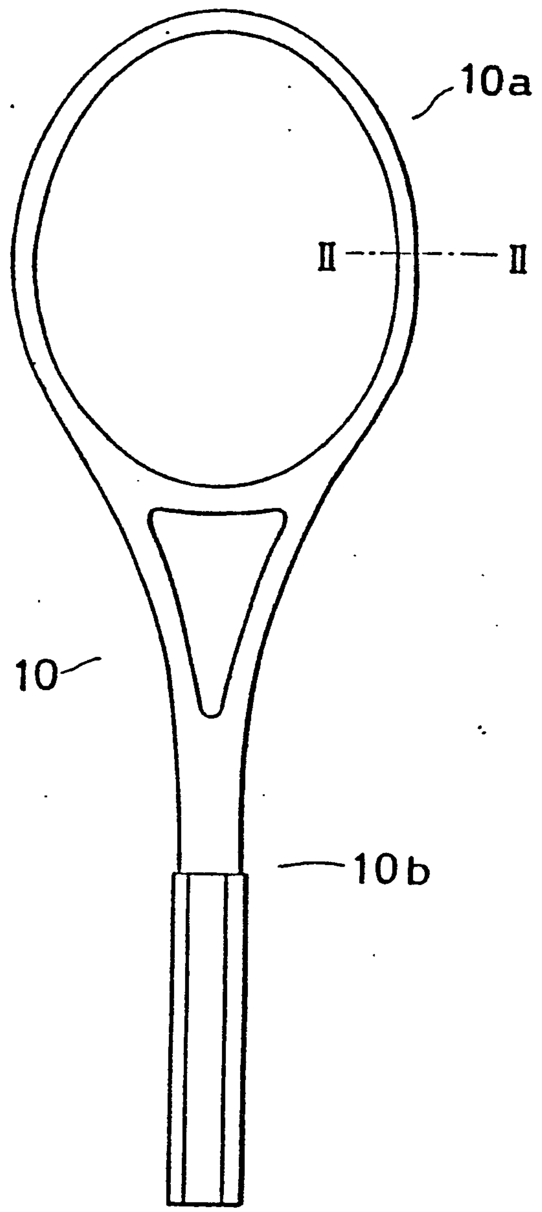


FIG. 12

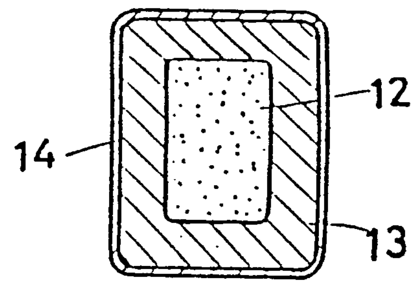


FIG. 13

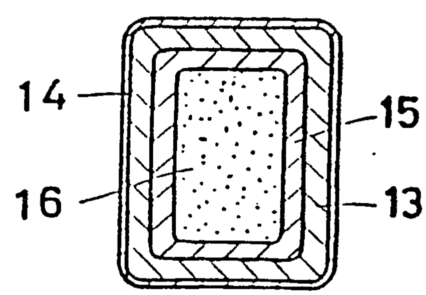
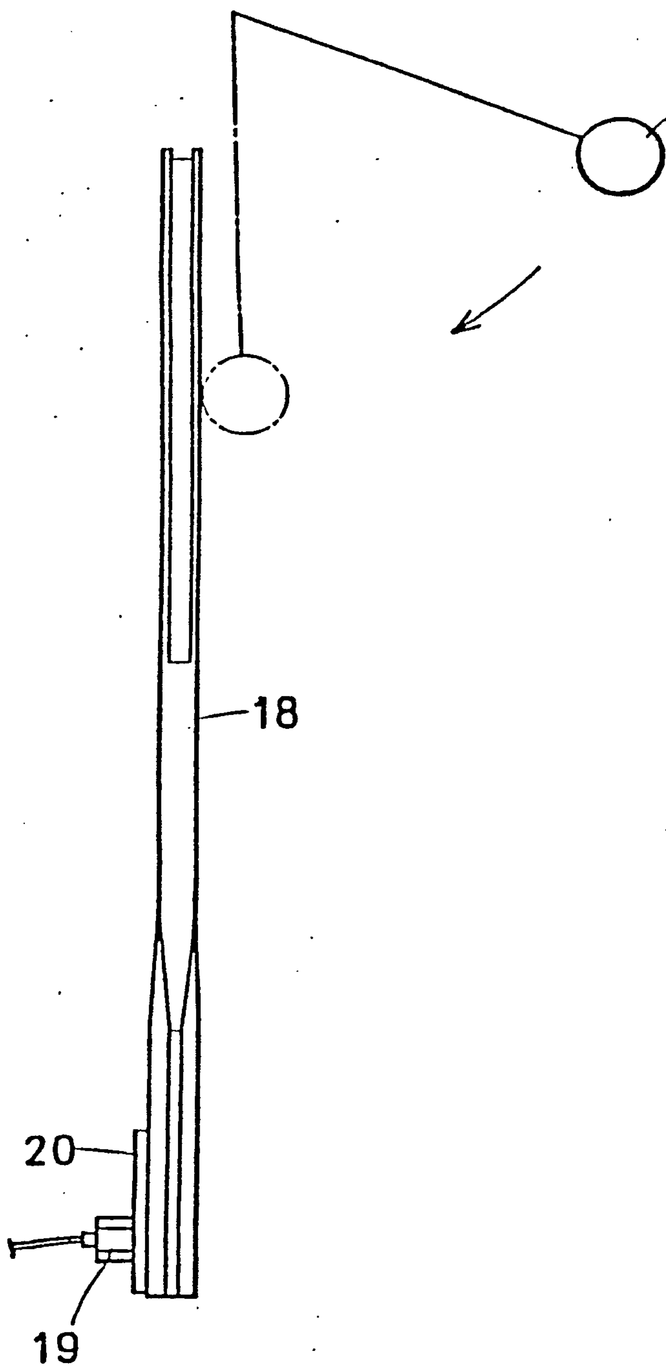
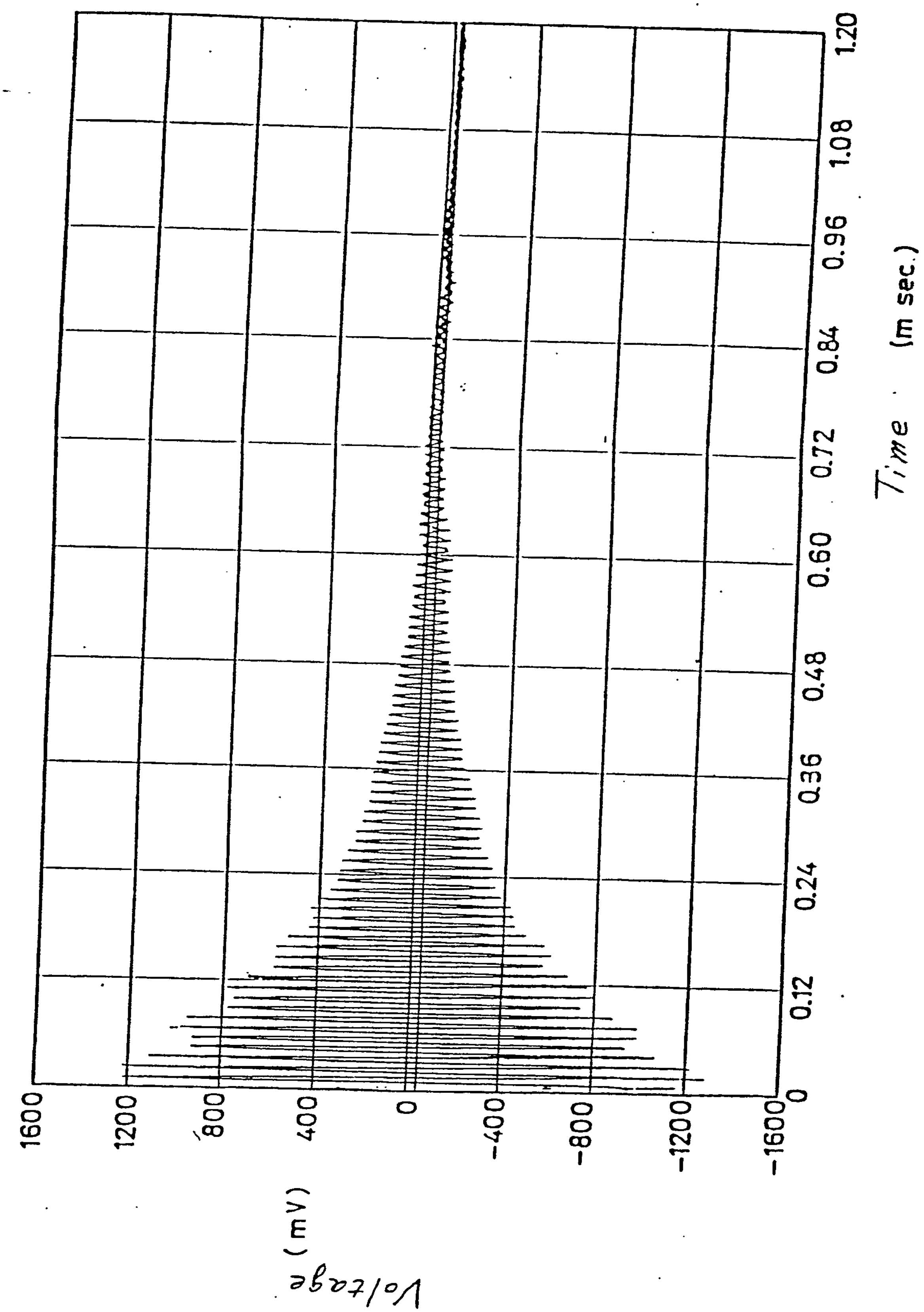


FIG. 14





1600
1200
800
400
0
-400
-800
-1200
-1600
Voltage (mV)
0
0.12
0.24
0.36
0.48
0.60
0.72
0.84
0.96
1.08
1.20
Time (m sec.)

FIG. 15

0231381

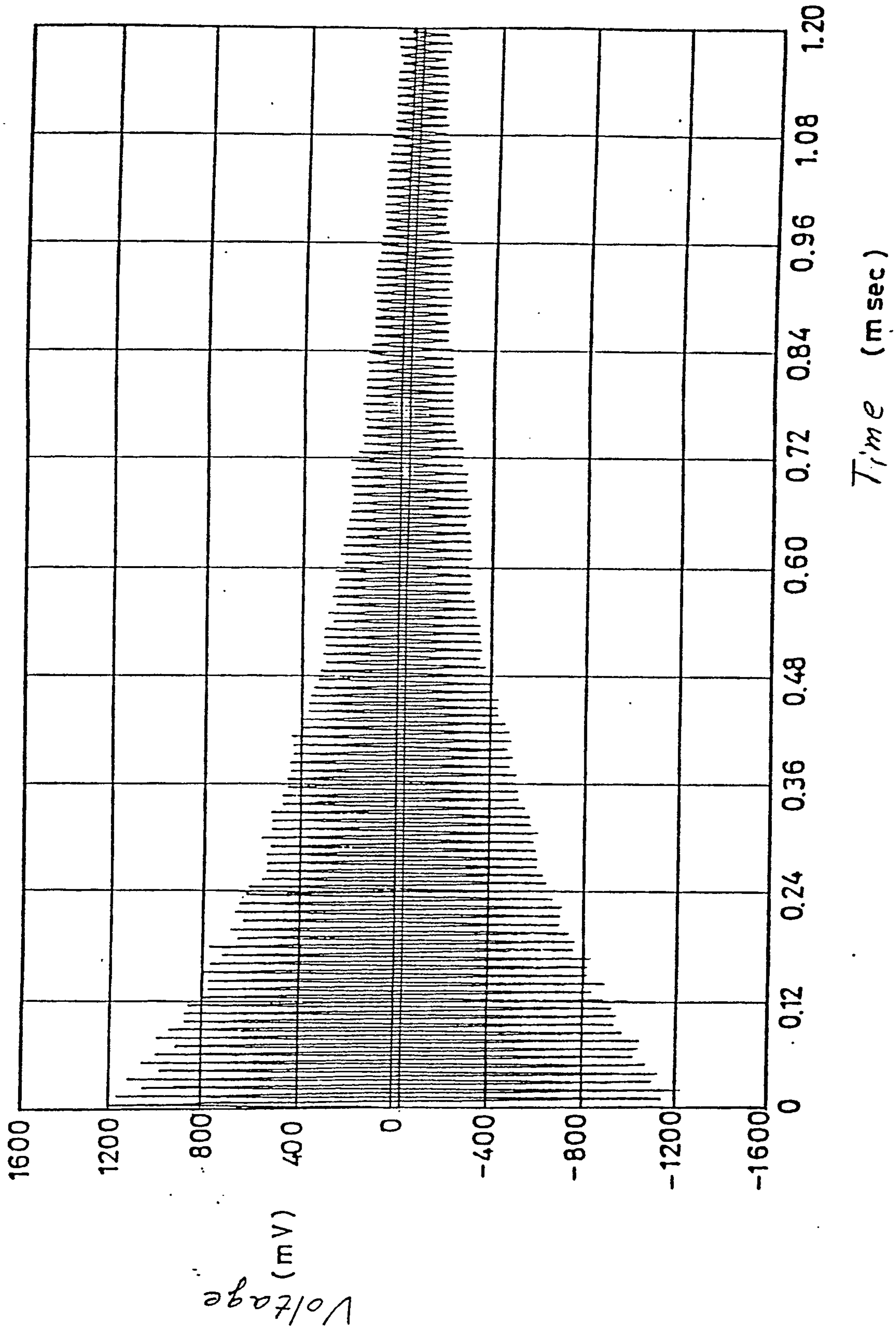


FIG. 16

INTERNATIONAL SEARCH REPORT

0231381

International Application No. PCT/JP86/00276

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl^4 B29C39/10

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	B29C39/10, 39/12, 39/18, 39/20

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

Jitsuyo Shinan Koho	1931 - 1986
Kokai Jitsuyo Shinan Koho	1971 - .1986

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	JP, A, 55-117630 (Toray Industries, Inc.) 10 September 1980 (10. 09. 80) & US, A, 4332767 & EP, A1, 13754 & EP, B1, 13754	1, 4
X	JP, A, 55-14205 (Toray Industries, Inc.) 31 January 1980 (31. 01. 80) (Family: none)	1
Y	JP, A, 55-117630 (Toray Industries, Inc.) 10 September 1980 (10. 09. 80) & US, A, 4332767 & EP, A1, 13754 & EP, B1, 13754	2,3,5, - 10

* Special categories of cited documents: [15]

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
August 22, 1986 (22. 08. 86)	September 1, 1986 (01. 09. 86)
International Searching Authority [1]	**Signature of Authorized Officer [20]**
Japanese Patent Office	

Form PCT/ISA/210 (second sheet) (October 1981)